



Review

Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts

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ABSTRACT

With the progressive increase in global energy demands and the continuous depletion of worldwide fossil resources, renewable lignocellulosic biomass has attracted more and more attention. As the most abundant component of lignocellulosic biomass, cellulose, which is a linear polymer formed by the repeating connection of glucose units through β -1,4-glycosidic linkages, is considered to be an inexhaustible raw material for the sustainable production of chemicals and fuels. For the effective utilization of cellulose, the primary and essential step is the hydrolysis of cellulose into glucose. Although homogeneous acids and cellulases are the most common catalysts for the hydrolysis of cellulose into glucose, they possess a series of problems such as reactor corrosion, waste treatment and poor recyclability and high cost, low efficiency and long reaction time, respectively. In order to overcome the above-mentioned drawbacks, solid acid catalysts have been increasingly employed for the hydrolysis of cellulose into glucose in recent years. In this review, the state-of-the-art studies on the hydrolysis of cellulose into glucose over various types of solid acid catalysts such as acid resins, metal oxides, H-form zeolites, heteropoly acids, functionalized silicas, supported metals, immobilized ionic liquids, carbonaceous acids and magnetic acids are systematically summarized. Meanwhile, reaction medias, auxiliary methods and neoteric strategies for the hydrolysis of cellulose into glucose are intensively discussed. Furthermore, some potential research trends in the future are also prospected to provide some valuable ideas for the hydrolysis of cellulose into glucose in a more green, simple, efficient and inexpensive way.

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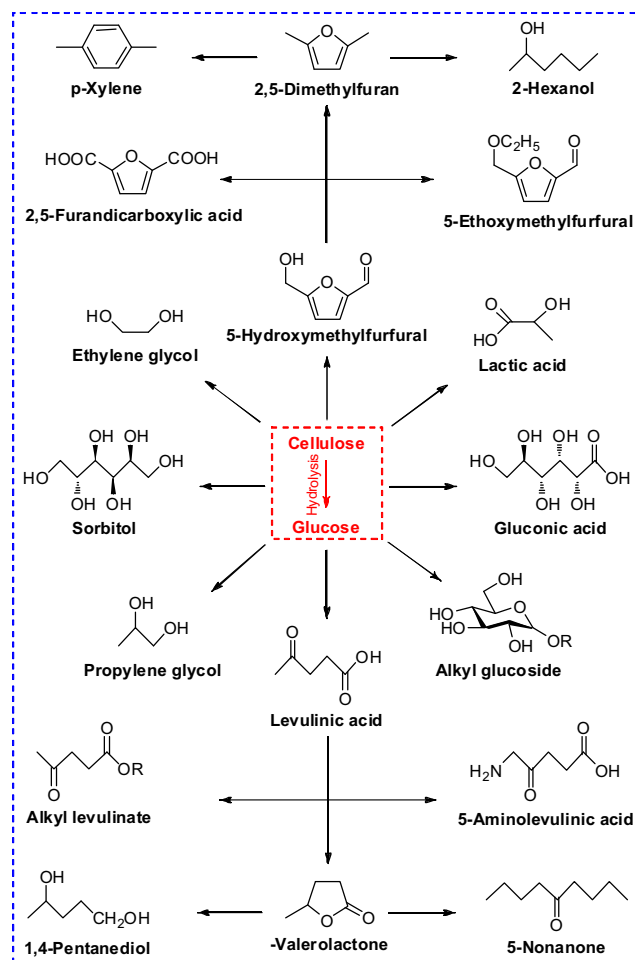
1. Introduction

Among various renewable resources, lignocellulosic biomass, possessing a range of excellent properties such as widespread, abundant, diverse and inexpensive, is regarded as a promising and appealing alternative to nonrenewable fossil resources [1–8]. As estimated, nature produces 200 billion metric tons of lignocellulosic biomass with an energy content of 3×10^{18} kJ year⁻¹ by photosynthesis, which is around 10 times the present and annual energy consumption of the world [9–12]. Under the drive of a huge potential of lignocellulosic biomass, many countries in the world have launched the corresponding research and development plans such as America's "Energy Farm", Brazil's "Alcohol Program", India's "Renewable Energy Scenario" and Japan's "Sunshine Project" [13]. As is known to all, cellulose is the most abundant component of lignocellulosic biomass [14–20], its effective utilization is of great importance to reduce the excessive dependence on fossil resources, alleviate the energy crisis and decrease the environmental pollution. In recent years, the selective transformation of cellulose into a variety of high-value chemicals and high-quality fuels (Scheme 1) has been becoming one of the most interesting and attractive issues in the field of biorefinery [21–34]. However, it should be pointed out that the hydrolysis of cellulose into glucose is the starting point and entry point of biorefinery [35–39], which is crucial to the whole selective transformation chain.

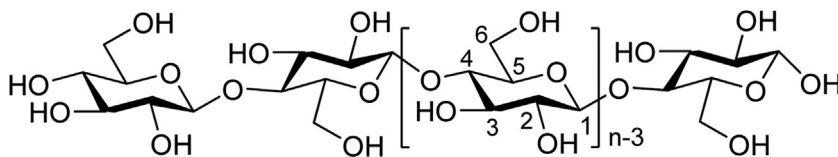
In a long period of time, considerable attention has been concentrated on homogeneous acids and cellulases for the hydrolysis of cellulose into glucose. Sulfuric acid (H₂SO₄), nitric acid (HNO₃), perchloric acid (HClO₄), phosphoric acid (H₃PO₄), hydrochloric acid (HCl), hydrofluoric acid (HF) and formic acid (FA) are known as a typical type of homogeneous acids [40–48]. Although they exhibit reasonable prices and good catalytic activities, their practical applications are difficult due to a lot of problems including reactor corrosion, waste treatment and poor recyclability as well as severe reaction temperature [49–54]. In contrast to homogeneous acids, cellulases that can be derived from *Trichoderma reesei*, *Aspergillus niger*, *Aspergillus nidulans* and *Penicillium funiculosum* are more selective and competitive to hydrolyze cellulose into glucose at lower reaction temperature [55–59]. However, enzymatic hydrolysis of cellulose is a slow process, which will spend a long time to achieve a satisfactory yield of glucose [60–62]. In addition, prior to enzymatic hydrolysis of cellulose into glucose, an energy- and cost-intensive pretreatment is needed to remove the recalcitrance to cellulases [63–65]. More unfortunately, cellulases are still very expensive in the present, making them unacceptable to pursue high hydrolysis rate by increasing the amount of cellulases [66–69]. From the viewpoint of green chemistry and industrialization, solid acid catalysts such as acid resins, metal oxides, H-form zeolites, heteropoly acids, functionalized silicas, supported metals, immobilized ionic liquids, carbonaceous acids and magnetic acids, which are separable, recoverable and reusable, should be the excellent choices for the hydrolysis of cellulose into glucose, because they

have a tremendous potential to overcome the above-mentioned limitations [16]. In other words, solid acid catalysts can open up an opportunity to explore more efficient, economical, simpler and greener processes for the hydrolysis of cellulose into glucose [50]. More gratifyingly, more and more interest has been devoted to the hydrolysis of cellulose into glucose by using various types of solid acid catalysts. In 2009 and 2013, Rinaldi and Schüth [35] and Huang and Fu [60] have reviewed some available advancements on the hydrolysis of cellulose into glucose with solid acid catalysts, respectively. However, this research field is progressing very fast and many significant findings are continuously observed. Hence, a real-time and comprehensive review is also needed.

In this review, in addition to summarizing the latest applications and achievements of solid acid catalysts, much special emphasis



Scheme 1. Selective transformation of cellulose into various chemicals and fuels via glucose.



Scheme 2. Structure of cellulose ($n = DP$, degree of polymerization) [72].

is put on other important aspects such as reaction medias, auxiliary methods and neoteric strategies for the hydrolysis of cellulose into glucose. The review is organized in the following order: reaction medias for the hydrolysis of cellulose; solid acid catalysts for the hydrolysis of cellulose; auxiliary methods for the hydrolysis of cellulose; and neoteric strategies for the hydrolysis of cellulose. Section 6 of this review provides some potential research trends on the hydrolysis of cellulose into glucose over solid acid catalysts.

2. Reaction medias for the hydrolysis of cellulose

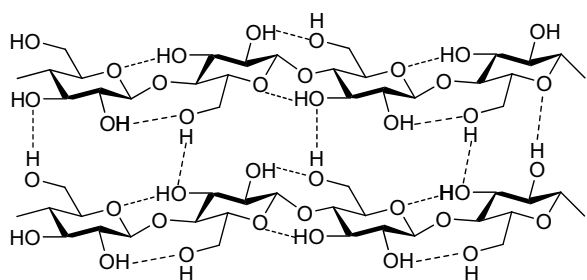
It is well-known that cellulose is a linear polymer consisting of many glucose units via β -1,4-glycosidic linkages (Scheme 2) [70–77], which was firstly discovered by Payen and Hebd in 1838 [78] and then elucidated by Staudinger in 1920 [79]. Due to the presence of a large number of hydroxyl ($-\text{OH}$) groups, there are numerous intramolecular and intermolecular hydrogen bonds in cellulose (Scheme 3) [80–84], leading to a intricate supramolecular structure and a strong mechanical strength. As a consequence, cellulose is insoluble in water and most common organic liquids [85–89], which result in a trouble in the dissolution of cellulose and the subsequent hydrolysis of cellulose into glucose. Therefore, the search for an appropriate solvent with a vigorous dissolving capacity is very important for the effective hydrolysis of cellulose into glucose. As reported in the previous studies, the derivatizing solvents such as sodium hydroxide/urea ($\text{NaOH}/\text{CO}(\text{NH}_2)_2$) [90] and sodium hydroxide/carbon disulfide (NaOH/CS_2) [80] and the non derivatizing solvents such as *N*-methylmorpholine-*N*-oxide monohydrate (NMO) [91], *N,N*-dimethylsulfoxide/tetrabutylammonium fluoride trihydrate (DMSO/TBAF) [92] and *N,N*-dimethylacetamide/lithium chloride (DMA/LiCl) [93] have been developed for the dissolution of cellulose. Although these solvents are applicable in industry, they are not environmental-friendly and sustainable due to the existence of toxicity, the insufficient of solvation or the absence of recyclability [81]. Based on the above facts, a greener and stronger alternative is warmly welcome (or perhaps is desperately needed!).

In recent years, as a novel class of solvents, ionic liquids, which are the unique ionic salts with the melting temperature lower than 100°C [94–97], have been considered to be more greener and stronger solvents in comparison of many traditional solvents, leading to numerous applications in a variety of fields [98], this is because that they have a sequence of special physicochem-

ical properties such as negligible vapor pressure, high thermal stability, broad electrochemical window, low flammability, high conductivity and close to infinite structural variation [99–103]. In 1934, Graenacher discovered that *N*-ethylpyridinium chloride in the presence of *N*-containing bases have the ability to dissolve cellulose with the formation of solutions [104], which should be the first example of the dissolution of cellulose by the use of ionic liquids [80]. Unfortunately, at that time, the practical importance of ionic liquids was not realized. Currently, a breakthrough was achieved in 2002, Swatloski et al. found that cellulose could be readily dissolved in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) without derivatization under a mild temperature of 100°C , and when this process was carried out in a microwave oven, a clear solution containing up to 25 wt% cellulose were obtained [87]. Subsequently, a wide range of other ionic liquids such as 1,1,3,3-tetramethylguanidine propionate ([TMGH][COOEt]) [105], 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) [82], 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) [106], 1-butyl-3-methylpyridinium chloride ([BMPy]Cl) [107], 1-butyl-3-methylimidazolium formate ([BMIM]HCOO) [108], 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) [109], 1-butyl-3-methylimidazolium acetate ([BMIM]OAc) [110], 1-butyl-3-methylimidazolium dicyanamide ([BMIM]DCA) [111], 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)imide ([EMIM]NTf₂) [112] and 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM](MeO)₂PO₂) [113] were also studied. Compared to traditional solvents, the remarkable dissolving power of ionic liquids is attributed to the hydrogen-bonding interactions between $-\text{OH}$ groups of cellulose and anions of ionic liquids [114–116], which has been proved by the technique of nuclear magnetic resonance (NMR) [115]. Moreover, the current results indicate that the solubility of cellulose in ionic liquids is closely related to the hydrogen bond accepting ability (basicity) of anions [108]. Namely, the higher the ability of anions to accept hydrogen bonds, the greater the capacity of ionic liquids to dissolve cellulose [81]. Hence, up to now, the most effective anions are identified to be OAc^- , Cl^- and HCOO^- [80]. In addition to the types of anions, the shorter alkyl chains, the stronger electron-withdrawing groups in cations and the weaker interactions between cations and anions also play an important role in improving the solubility of cellulose in ionic liquids, the detailed studies have been reviewed by Sun et al. [75], Mäki-Arvela et al. [114] and Brandt et al. [116]. According to the above descriptions, it is concluded that ionic liquids have a tremendous potential to disrupt numerous intramolecular and intermolecular hydrogen bonds of cellulose for the dissolution of cellulose, they can be used as excellent solvents for the hydrolysis of cellulose into glucose. However, it is worth noting that the quantitative recovery and reuse of ionic liquids should be mandatory due to high cost of ionic liquids in the present technologies [35].

3. Solid acid catalysts for the hydrolysis of cellulose

At present, an increasing number of solid acid catalysts have been designed and used for the hydrolysis of cellulose. In this part, several typical types of solid acid catalysts and their catalytic activities are summarized in Table 1.



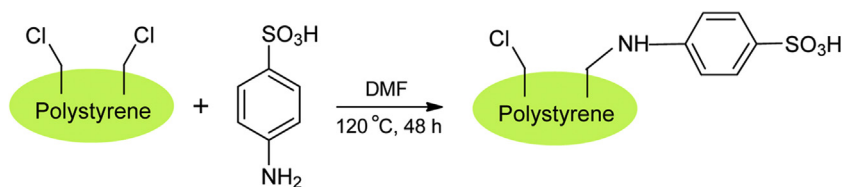
Scheme 3. Intermolecular and intramolecular hydrogen bonds in cellulose [81].

Table 1
Hydrolysis of cellulose over various solid acid catalysts^a.

Catalyst	Pretreatment method	Solvent	Catalyst loading (%)	Cellulose concentration (%)	Temperature (°C)	Time (h)	TRS yield (%)	Glucose yield (%)	References
Amberlyst-15	–	[BMIM]Cl	20.0	5.0	130	5	25.0	–	[118]
Nafion-NR50	–	H ₂ O	50.0	1.0	160	4	–	16.0	[121]
Nafion-SAC-13	D/R	H ₂ O	47.0	6.7	190	24	–	9.0	[122]
CP-SO ₃ H	–	H ₂ O	492.5	10.0	120	10	–	93.0	[66]
PAA-b-PSSH	BM	H ₂ O	648.0 ^b	1.0	120	2	–	10.0	[124]
PAA-r-PSSH	BM	H ₂ O	648.0 ^b	1.0	120	2	–	35.0	[124]
HNbMoO ₆	–	H ₂ O	200.0	2.0	130	12	8.5	–	[129]
Zn–Ca–Fe	–	H ₂ O	45.0	1.0	160	20	–	29.5	[130]
Zr/P/O	–	H ₂ O	100.0	5.0	150	10	–	5.8	[131]
Zr/P/O	–	H ₂ O	100.0	5.0	200	2	–	21.0	[131]
HY	–	[BMIM]Cl	11.1 ^b	5.0	130	2	–	50.0	[143]
Hβ	–	[BMIM]Cl	11.1 ^b	5.0	130	2	–	41.5	[143]
HZSM-5	–	[BMIM]Cl	11.1 ^b	5.0	130	1	–	18.1	[143]
H ₃ PW ₁₂ O ₄₀	–	H ₂ O	12.9 ^b	2.0	180	2	–	50.5	[152]
H ₅ BW ₁₂ O ₄₀	BM	H ₂ O	226.8 ^b	5.0	60	24	–	77.0	[153]
H ₅ AlW ₁₂ O ₄₀	BM	H ₂ O	226.8 ^b	5.0	60	24	–	68.0	[153]
H ₅ GaW ₁₂ O ₄₀	BM	H ₂ O	226.8 ^b	5.0	60	24	–	62.0	[153]
H ₆ CoW ₁₂ O ₄₀	BM	H ₂ O	226.8 ^b	5.0	60	24	–	59.0	[153]
Cs ₁ H ₂ PW ₁₂ O ₄₀	–	H ₂ O	9.7 ^b	2.0	160	6	30.1	27.2	[155]
Cs _{2.2} H _{0.8} PW ₁₂ O ₄₀	–	H ₂ O	9.7 ^b	2.0	160	6	17.5	16.2	[155]
C ₁₆ H ₂ PW	–	H ₂ O	11.3 ^b	1.4	170	8	–	39.3	[156]
[MIMPSH]H ₂ PW ₁₂ O ₄₀	–	H ₂ O/MIBK	11.3 ^b	1.8	140	5	40.2	36.0	[157]
[MIMPSH] ₃ PW ₁₂ O ₄₀	–	H ₂ O	5.8 ^b	1.3	180	3	34.0	21.0	[158]
Si ₃ C ₆₆ -823-SO ₃ H	BM	H ₂ O	100.0	1.0	150	24	–	50.4	[164]
CoFe ₂ O ₄ @SiO ₂ -SO ₃ H	–	H ₂ O	100.0	10.0	150	3	30.2	7.0	[165]
SBA-15-SO ₃ H	D/R	H ₂ O	150.0	6.7	150	3	–	52.0	[166]
MCM-41-SO ₃ H	–	H ₂ O	15.0	3.3	230	1/4	47.2	–	[167]
PSFSI-MSMA ₁₅ /SiO ₂	–	[BMIM]Cl	10.0 ^b	5.3	120	2	67.0	–	[168]
Ru/CMK-3	BM	H ₂ O	15.4	0.8	230	1/4	40.0	–	[176]
AIL-SiO ₂	–	H ₂ O	10.8 ^b	1.5	190	2	48.1	21.9	[182]
PrSO ₃ H-SiO ₂	–	H ₂ O	10.8 ^b	1.5	190	2	19.9	11.3	[182]
BC-SO ₃ H-IL-Zn	–	H ₂ O	50.0	13.3	90	2	58.7	–	[183]
AC-SO ₃ H	BM	H ₂ O	111.1	0.9	150	24	–	40.5	[140]
GO-ene	–	H ₂ O	111.1	1.0	150	24	–	49.9	[49]
GC-SO ₃ H	–	[BMIM]Cl	60.0	5.0	110	4	72.7	–	[196]
SC-SO ₃ H	–	[BMIM]Cl	100.0	2.5	120	4	71.0	–	[197]
SUCRA-SO ₃ H	D/R	H ₂ O	200.0	1.3	120	24	–	55.0	[203]
PVC-SC-SO ₃ H	PA	H ₂ O	200	1.0	120	6	94.2	–	[204]
HA-CC-SO ₃ H	–	H ₂ O	25.0	0.5	155	4	–	10.8	[51]
AC-N-SO ₃ H-250	BM	H ₂ O	111.1	1.0	150	24	–	62.6	[17]
CMK-3	BM	H ₂ O	111.1	1.0	150	24	–	74.5	[17]
Fe ₃ O ₄ -SBA-SO ₃ H	D/R	H ₂ O	150.0	6.7	150	3	–	50.0	[36]
Fe ₃ O ₄ @SiO ₂ -SO ₃ H	–	[BMIM]Cl	62.5	8.0	130	8	73.2	–	[206]
Fe ₃ O ₄ @C-SO ₃ H	BM	H ₂ O	300.0	0.5	140	12	–	25.3	[207]
PCM-SO ₃ H	–	[BMIM]Cl	100.0	5.0	130	3	68.9	–	[37]
PCM-SO ₃ H	–	H ₂ O	20.0	1.0	180	9	51.0	–	[37]
Fe-GO-SO ₃ H	–	H ₂ O	100.0	1.0	75	44	94.3	50.0	[208]
Mg ₄ Al ₂ (OH) ₁₂ CO ₃	BM	H ₂ O	111.1	0.3	150	24	47.4	–	[209]
CaFe ₂ O ₄	D/R	H ₂ O	111.1	0.3	150	24	49.8	–	[210]
SA-MMT	–	H ₂ O	200.0	3.6	200	4	6.9	–	[211]
PA-MMT	–	H ₂ O	200.0	3.6	200	4	16.9	–	[211]
MIL-101-PCP-SO ₃ H	BM	H ₂ O	800.0	1.3	120	3	–	1.4	[212]
PIL-CM-PSSA	–	H ₂ O	–	1.0	140	48	32.7	–	[63]
PIL-CM-PSSA	–	[EMIM]Cl	–	1.0	130	6	97.4	–	[63]

^a BM, D/R and PA are representative of ball-milling, dissolution/regeneration and phosphoric acid, catalyst loading and cellulose concentration are relative to the mass of cellulose and the mass of solvent, respectively.

^b Catalyst loading is relative to the mole of glucose units in cellulose.

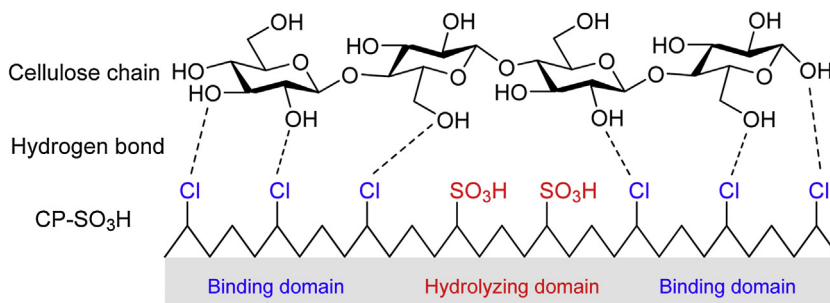
Scheme 4. Synthesis of CP-SO₃H [66].

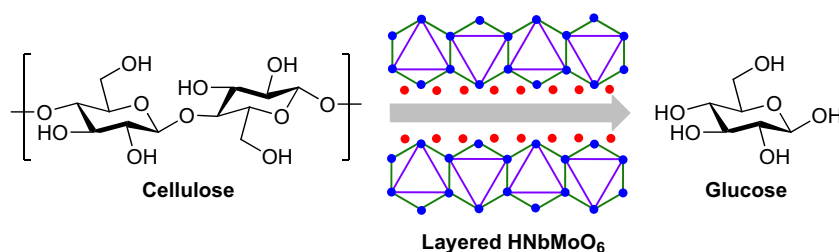
3.1. Acidic resins

It is generally known that resins are composed of organic polymers, containing the macroreticular structures with high specific surface areas and high ion-exchange capacities, their acidities are mainly due to the presence of sulfonic ($-\text{SO}_3\text{H}$) groups [50]. As early as the 1962, acidic resins such as Amberlite-IR-120 and Dowex-50 (styrene-based polymers) have been used by Hartler and Hyllengren in the hydrolysis of cellulose [117]. Unfortunately, the expected results were not obtained. Recent pioneering work on the hydrolysis of cellulose was reported by Rinaldi et al. in which Amberlyst-15 (styrene-divinylbenzene-based polymer) was applied in the presence of [BMIM]Cl [118]. In this hydrolysis process, cellulose was primarily dissolved in [BMIM]Cl, and then it was selectively hydrolyzed by Amberlyst-15 at 100 °C. After 1.5 h, cellooligomers with a DP around 30 were observed, and then precipitated in high yield of 90.0% by the addition of water. More interestingly, the amount of reducing sugars was negligible during the first 1.5 h, which was in accordance with the induction period required for the release of reducing sugars. As reported, the solubility of reducing sugars is very high in ionic liquids [111], making the separation of reducing sugars and the recovery of ionic liquids extremely difficult. However, this catalytic process gave a feasibility to hydrolyze cellulose into cellooligomers instead of reducing sugars, which was the most appealing part of this process. Furthermore, it should be pointed out that the generated cellooligomers could be further hydrolyzed into reducing sugars even glucose with the extension of reaction time. That is to say, if this catalytic process was terminated at the proper time, cellooligomers, reducing sugars or glucose could be selectively obtained for various utilization in biorefinery. For a better understanding of the controlling factors in hydrolysis of cellulose over Amberlyst-15 in [BMIM]Cl, a range of parameters were investigated by Rinaldi et al. [119]. The results demonstrated that the initial size of cellulose chains was crucial in the control of product distribution, and large chains were preferably hydrolyzed into smaller ones (cellooligomers) instead of producing reducing sugars or glucose, which well explained the induction period. Moreover, the results also revealed that the induction period heavily depended on the amount of Amberlyst-15 used for the hydrolysis reaction, and when the amount of Amberlyst-15 equivalent to H^+ increased from 0.46 mmol to 6.9 mmol, the induction period decreased from 1.9 h to less than 5 min, meaning that

the amount of Amberlyst-15 played an important role in the hydrolysis of cellulose. Furthermore, it is particularly necessary to point out that H^+ was released from the Brønsted acid sites of Amberlyst-15 through ion-exchange with the cations of [BMIM]Cl, it was proved to be the real catalyst in the hydrolysis of cellulose [119]. In principle, the homogeneous nature of Amberlyst-15 as a solid acid can be extended to other solid acid catalysts with the Brønsted acid sites. For any such catalyst, the ion-exchange process, resulting in the release of H^+ , will proceed in the presence of ionic liquids to some extent. However, it is worth noting that Amberlyst-15 has a main drawback that is the poor thermal stability, this is because that the design temperature of Amberlyst-15 is lower than 130 °C, above which the removal of Brønsted acid sites will lead to the deactivation of the catalyst [120]. In comparison of Amberlyst-15, Nafion-NR50 and Nafion-SAC-13 (tetrafluoroethylene-based polymers) have the very similar acidic characters, however, they show the better thermal stabilities. When cellulose was hydrolyzed in aqueous solution by Nafion-NR50 and Nafion-SAC-13, the yields of glucose with 16.0% and 9.0% were achieved at 160 °C for 4 h [121] and 190 °C for 24 h [122], respectively.

More excitingly, the catalytic activities of acidic resins can be improved by loading other functional groups on the resin materials [74]. In order to imitate the enzymatic hydrolysis of cellulose, a novel acidic resin (CP-SO₃H) containing cellulose-binding sites and cellulose-hydrolyzing sites was synthesized through molecular design by Shuai and Pan in 2012 (Scheme 4) [66]. To be more precise, a chloromethyl polystyrene resin was firstly chosen as the catalyst support, and then, $-\text{SO}_3\text{H}$ groups were introduced by partially substituting $-\text{Cl}$ groups with sulfanilic acid. In this catalyst, $-\text{Cl}$ groups played the cellulose-binding role by forming hydrogen bonds with $-\text{OH}$ groups of cellulose and $-\text{SO}_3\text{H}$ groups played the cellulose-hydrolyzing role by breaking β -1,4-glycosidic linkages of cellulose. When CP-SO₃H was used for the hydrolysis of cellulose in aqueous solution, glucose with a yield of 93.0% was achieved at a moderate reaction temperature of 120 °C for 10 h, this excellent result was ascribed to the synergistic effect of $-\text{Cl}$ groups and $-\text{SO}_3\text{H}$ groups (Scheme 5) [66]. Furthermore, the activation energy was 83.0 kJ mol⁻¹ that was significantly smaller than 174.7 kJ mol⁻¹ in the presence of H_2SO_4 [123], which might also explain why the hydrolysis of cellulose in the presence of CP-SO₃H could be conducted at a moderate reaction temperature. In the same way, poly(acrylic acid)-block-poly(styrene sulfonic acid)

Scheme 5. Synergistic effect of $-\text{Cl}$ groups and $-\text{SO}_3\text{H}$ groups [66].



Scheme 6. Hydrolysis of cellulose to glucose with HNbMoO_6 [129].

(PAA-*b*-PSSH) and poly(acrylic acid)-random-poly(styrene sulfonic acid) (PAA-*r*-PSSH) containing cellulose-binding sites ($-\text{COOH}$) and cellulose-hydrolyzing sites ($-\text{SO}_3\text{H}$) were successfully prepared by initiatory living radical polymerization and subsequent thermolysis [124]. Interestingly, PAA-*r*-PSSH displayed a higher catalytic activity, the yield of glucose with 35.0% was obtained in aqueous solution at 120 °C for 2 h. However, under the same reaction conditions, only 10.0% glucose yield was observed when PAA-*b*-PSSH was used as a catalyst. It is predicted that the random copolymer could make much of active sites than the block copolymer because the more dispersive active sites in the chain of random copolymer could hydrolyze cellulose more efficiently [124]. Nevertheless, a more comprehensive study should be conducted to investigate the details.

3.2. Metal oxides

Metal oxides are classified into single metal oxides and complex metal oxides, their porous structures allow the access of reactants to contact the active acid sites inside the pores [60]. Up to now, many metal oxides such as niobium pentoxide (Nb_2O_5) [125], niobium phosphate (NBP) [125], tantalum molybdate (HTaMoO_6) [126], zirconium tungstate (WO_3/ZrO_2) [127] and niobium tungstate ($\text{Nb}_2\text{O}_5/\text{WO}_3$) [128] have been widely applied for the hydrolysis of cellobiose. However, only a small number of metal oxides were directly used for the hydrolysis of cellulose.

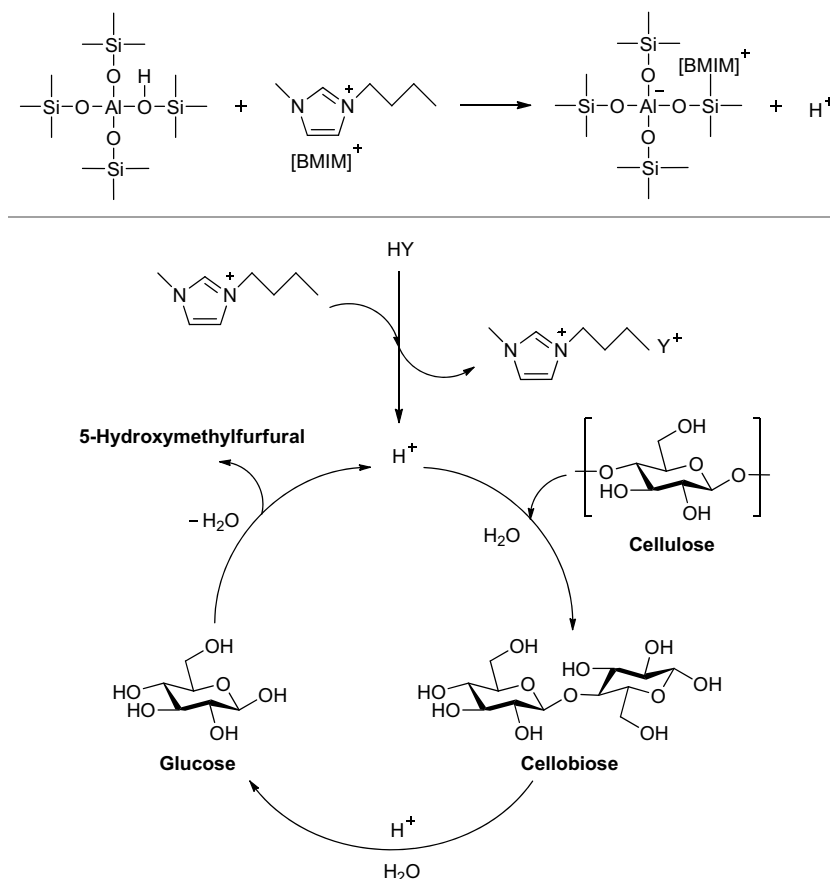
In 2008, a layered transition-metal oxide (HNbMoO_6) was prepared by Takagaki et al. and used for the hydrolysis of cellulose in aqueous solution (Scheme 6) [129]. Compared to Amberlyst-15, it produced two times in the yield of reducing sugars at 130 °C for 12 h. The high catalytic activity of HNbMoO_6 was due to its strong acidity, water tolerance and intercalation ability. Relative to glucose, the production of cellobiose over HNbMoO_6 was preferential, which was probably attributed to the difference of intercalation behavior between glucose and cellobiose. Moreover, the authors pointed out that the yield of reducing sugars could be further improved by increasing the surface area of catalyst or by dissolving cellulose in an ionic liquid [129]. Subsequently, Zhang et al. reported a nanoscale metal oxide catalyst ($\text{Zn}-\text{Ca}-\text{Fe}$), it also exhibited a good catalytic activity for the hydrolysis of cellulose [130]. When this hydrolysis reaction was conducted in aqueous solution, the conversion of cellulose and the selectivity of glucose were up to 42.6% and 69.2% at 160 °C for 20 h, respectively. In addition, it is worth noting that $\text{Zn}-\text{Ca}-\text{Fe}$ is paramagnetic because of the presence of iron, and so it has a large potential to be separated from reaction mixture by an external magnet. More recently, a series of complex metal oxides such as silica-zirconia ($\text{Si}/\text{Zr}/\text{O}$), sulfated silica-zirconia ($\text{Sulf}-\text{Si}/\text{Zr}/\text{O}$), zirconium phosphate ($\text{Zr}/\text{P}/\text{O}$), sulfonated-zirconium phosphate ($\text{Sulf}-\text{Zr}/\text{P}/\text{O}$), Nafion incorporated silica ($\text{Nafion}-\text{SiO}_2$), trifluoromethanesulfonic acid grafted zirconia ($\text{TFA}-\text{ZrO}_2$) and stannic-tungstate ($\text{Sn}/\text{W}/\text{O}$) were synthesized by Gliozzi et al. and their catalytic activities for the hydrolysis of cellulose were compared [131]. Among them, $\text{Zr}/\text{P}/\text{O}$ showed

an interesting behavior with a high selectivity to glucose, hence, a more detailed study was further performed. The results indicated that 5.8% glucose yield with negligible formation of decomposition products was observed at 150 °C for 10 h, and when the reaction temperature was elevated to 200 °C, a good yield of glucose with 21.0% was achieved in a shorter reaction time of 2 h. Furthermore, quite unexpectedly, when $\text{Zr}/\text{P}/\text{O}$ was employed as a catalyst for the hydrolysis of cellobiose, glucose yield as high as 97.0% was obtained at 150 °C for 2 h, this outstanding catalytic activity was ascribed to its high affinity to β -1,4-glucans [131].

3.3. H-form zeolites

Zeolites are a unique class of crystalline aluminosilicates whose structures are formed by the tetrahedra of SiO_4 and AlO_4 , which are connected through the corner-sharing oxygen atoms, forming three-dimensional frameworks with well-defined channels or cavities [132–134]. Furthermore, it should be noted that zeolites possess Brønsted base sites and Lewis acid sites, which are caused by the bridging $\text{Si}-\text{OH}-\text{Al}$ groups and three-fold coordinated lattice-Al centers, respectively [135–137]. Owing to tunable acidities, superior thermostabilities and excellent shape-selectivities [137–139], zeolites have been successfully used for the hydrolysis of cellulose in the past few years. In 2008, Onda et al. found that H β and HZSM-5 with a high Si/Al ratio of 75 and 45 showed the higher catalytic activities for the production of glucose in aqueous solution than H-mordenite with a low Si/Al ratio of 10, respectively, which was in contrast to the acid densities of zeolites [140]. When the ratio of Si/Al was uniformly set as 50, H-mordenite and H-faujasite were confirmed to be more active than HZSM-5 for the hydrolysis of cellulose in the mixture of water and [BMIM]Cl [141]. As everyone knows, H-mordenite and H-faujasite have a twelve-member ring structure with a large pore size around 0.7–0.8 nm, however, the structure of HZSM-5 is ten-member ring and the pore size is around 0.5 nm. The active sites of zeolites are in the pores so that the active sites of cellulose (β -1,4-glycosidic linkages) must enter the pores to contact the active sites of zeolites for the hydrolysis of cellulose [74]. In this case, the larger pore size is preferred [142], this may explain why the twelve-member ring of zeolites are more effective than ten-member ring of zeolites. As can be seen from the above results, the catalytic activities of zeolites in the hydrolysis of cellulose are largely affected by Si/Al ratios and pore structures of zeolites.

More recently, to explore the nature of zeolite-promoted hydrolysis of cellulose in ionic liquids and to provide the direct insight into the mutual interactions of zeolites and ionic liquids in the hydrolysis of cellulose, HY and [BMIM]Cl were taken as a combination and a sequence of physical and chemical characterizations were conducted by Cai et al. [143]. The results of X-ray diffraction (XRD) suggested that the framework structure of HY was particularly stable in [BMIM]Cl while the cell parameter was enlarged due to the dilatation effect of [BMIM]Cl, and the results of elemental analysis and Fourier transform infrared spectrum (FT-



Scheme 7. Reaction pathway for the hydrolysis of cellulose over HY in [BMIM]Cl [143].

IR) demonstrated that the Brønsted acid sites of HY were released in the form of H⁺ via ion-exchange with the cations of [BMIM]Cl, which was accordance with the results of Rinaldi et al. [119], however, the Lewis acid sites of HY were more stable in the reaction process. That is to say, although the Lewis acid sites of HY may work in the hydrolysis of cellulose, the main active species should be the Brønsted acid sites. On the basis of the characterizations, the authors proposed a plausible reaction pathway for the hydrolysis of cellulose over HY in [BMIM]Cl (Scheme 7) [143]. Initially, HY in [BMIM]Cl could allow [BMIM]⁺ enter the inner channel of HY and then [BMIM]⁺ was anchored in HY via chemical interaction. Subsequently, [BMIM]⁺ exchanged with the Brønsted acid sites of HY to release H⁺, which could readily catalyze the hydrolysis of cellulose into glucose. Moreover, by adding water gradually into [BMIM]Cl as the reaction progress, HY with the catalyst loading of 11.1 mol% led to a yield of glucose with 50.0% at 130 °C for 2 h [143].

3.4. Heteropoly acids

Heteropoly acids are made up of a particular combination of hydrogen cations and polyoxometalate anions [50]. The most common heteropoly acids are Keggin type acids with the anions of [XM₁₂O₄₀]ⁿ⁻, which are composed of a central tetrahedron XO₄ surrounded by twelve edge- and corner-sharing metal-oxygen octahedra MO₆, and where X is the heteroatom such as phosphorus and silicon and M is the addendum atom such as molybdenum and tungsten [144–147]. Unlike the above-mentioned catalysts, heteropoly acids have the discrete and mobile ionic structures and the proper redox abilities in addition to strong Brønsted acidities [148–150]. Due to these fascinating architectures and excellent properties, heteropoly acids have received much atten-

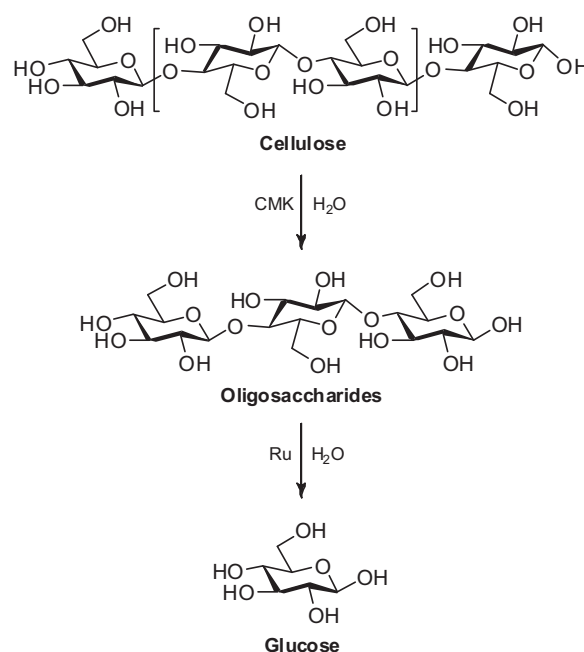
tion in the hydrolysis of cellulose. In 2009, HClO₄, H₂SO₄ and H₃PO₄ were employed to compare the catalytic activities of heteropoly acids such as phosphotungstic acid (H₃PW₁₂O₄₀) and silicotungstic acid (H₄SiW₁₂O₄₀) for the hydrolysis of cellulose, the results revealed that the yield of total reducing sugars (TRS) in aqueous solution decreased in the following order: H₃PW₁₂O₄₀ > H₄SiW₁₂O₄₀ > HClO₄ > H₂SO₄ > H₃PO₄, which was in line with the deprotonation enthalpies of these catalysts, indicating that a stronger Brønsted acidity is more favorable for the hydrolysis of β-1,4-glycosidic linkages in cellulose [151]. Soon afterwards, Tian et al. optimized the hydrolysis reaction conditions with the catalyst of H₃PW₁₂O₄₀ such as reaction time, reaction temperature, catalyst loading and cellulose amount, a high yield and selectivity of glucose with 50.5% and 92.3% were achieved in aqueous solution at 180 °C for 2 h with a mass ratio of cellulose to catalyst of 0.42, respectively [152]. More significantly, the salts of H₃PW₁₂O₄₀ (M_{3/n}PW₁₂O₄₀, M=Ca²⁺, Co²⁺, Y³⁺, Sn⁴⁺, Sc³⁺, Ru³⁺, Fe³⁺, Hf⁴⁺, Ga³⁺ and Al³⁺) were investigated by Shimizu et al. for the hydrolysis of cellulose, the results demonstrated that the hydrolysis rate of cellulose increased with the Lewis acidity of cations, while the selectivity of TRS was highest over cations with the moderate Lewis acidity such as Sn⁴⁺ and Ru³⁺ [151]. Apart from the above heteropoly acids, a suite of highly negatively charged heteropoly acids such as borotungstic acid (H₅BW₁₂O₄₀), aluminotungstic acid (H₅AlW₁₂O₄₀), gallotungstic acid (H₅GaW₁₂O₄₀) and cobaltotungstic acid (H₆CoW₁₂O₄₀) have also been developed to catalyze the hydrolysis of cellulose, resulting in 77.0%, 68.0%, 62.0% and 59.0% glucose yields at a low reaction temperature of 60 °C for 24 h, respectively, which were much higher than that over H₃PW₁₂O₄₀ [153]. After the characterization of XRD, the remarkable catalytic activities of these highly negatively charged heteropoly acids in

aqueous solution were proved to be attributed to their strong hydrogen-bond accepting abilities from the external oxygen atoms of anions, leading to a decrease in the crystallinity of cellulose.

It can be seen from the upper findings that heteropoly acids and their salts displayed good catalytic activities for the hydrolysis of cellulose, however, they can not be used as solid acid catalysts because of their high solubility in water. Fortunately, the hydrogen protons of heteropoly acids can be substituted by larger monovalent cations to generate solid acid catalysts that are insoluble in water [154]. Recently, Tian et al. found that the substitution of H^+ of $H_3PW_{12}O_{40}$ with Cs^+ could produce a series of cesium phosphotungstates ($Cs_xH_{3-x}PW_{12}O_{40}$, $x = 1-3$) and the various content of Cs would affect the catalytic activities for the hydrolysis of cellulose in aqueous solution [155]. Among the resulting $Cs_xH_{3-x}PW_{12}O_{40}$, $Cs_1H_2PW_{12}O_{40}$ showed the highest yield of glucose with 27.2% at 160 °C for 6 h, which was due to its strong protonic acid sites, while $Cs_{2.2}H_{0.8}PW_{12}O_{40}$ exhibited the highest selectivity of glucose with 83.9% under the same reaction conditions, which was ascribed to its microporous structure. Furthermore, another appealing route to generate solid acid catalysts is the development of the hybrid heteropoly acids. In 2011, an amphiphilic micellar heteropoly acid ($[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$, $C_{16}H_2PW$) was prepared by the reaction of hexadecyltrimethylammonium bromide (CTAB) and $H_3PW_{12}O_{40}$ [156], when it was used as a catalyst for the hydrolysis of cellulose in aqueous solution, 39.3% glucose yield with 89.1% glucose selectivity was obtained at 170 °C for 8 h. In addition, IR spectrum and MAS NMR spectroscopy of ^{31}P and ^{13}C confirmed that the interactions occurred between the oxygen atoms of cellulose and the terminal oxygen atoms of the amphiphilic micellar $C_{16}H_2PW$ [156], resulting in the accumulation of cellulose on the catalyst, which could improve the solubility of cellulose in water, overcome the diffusion of solid-solid reaction and promote the hydrolysis rate of cellulose. Following this work, an ionic liquid heterozygous heteropoly acid ($[MIMPSH]H_2PW_{12}O_{40}$) was synthesized in 2014 by the reaction of 1-(3-sulfonic acid)-propyl-3-methyl imidazole (MIMPSH) and $H_3PW_{12}O_{40}$, leading to 55.1% cellulose conversion and 36.0% glucose yield in the mixture of water and methyl isobutyl ketone (MIBK) at 140 °C for 5 h [157]. What is noteworthy is that this kind of catalyst contains the Brønsted acidity from the part of heteropoly acid, which favors the hydrolysis of cellulose. Moreover, the cation part acts like an ionic liquid, which can promote the dissolution of the cellulose. Using an analogous method, $[MIMPSH]_3PW_{12}O_{40}$ was also prepared and used for the hydrolysis of cellulose in aqueous solution, the yield of glucose with 21.0% was gained at 180 °C for 3 h [158].

3.5. Functionalized silicas

Silicas are a kind of inorganic materials with a wide range of porosities, which can be divided into amorphous silicas (SiO_2) and crystalline silicas (such as SBA-15 and MCM-41) [50]. It should be noted that SiO_2 , SBA-15 and MCM-41 are not appropriate as the catalysts for the hydrolysis of cellulose, because their intrinsic acidities are very weak even negligible. However, these materials can be modified by the introduction of $-SO_3H$ groups or other active groups [159–163]. In 2010, a sulfonated silica-carbon nanocomposite ($Si33C66-823-SO_3H$) was successfully developed as a solid acid catalyst for the hydrolysis of cellulose in aqueous solution, 50.4% glucose yield was achieved at 150 °C for 24 h [164]. The high activity of $Si33C66-823-SO_3H$ could be due to the presence of strong and accessible Brønsted acid sites and the hybrid structure constituted by interpenetrated silicas and carbon components, facilitating the adsorption of cellulose on solid acid catalyst. In the next year, Takagaki et al. prepared a cobalt ferrite-embedded silica nanocatalyst with $-SO_3H$ groups ($CoFe_2O_4@SiO_2-SO_3H$), and when it was applied for the hydrolysis

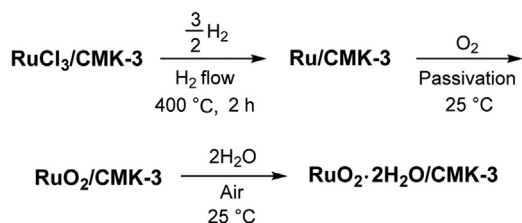


Scheme 8. Hydrolysis of cellulose into glucose by Ru/CMK-3 [176].

of cellulose in aqueous solution, the yield of TRS with 30.2% was obtained at 150 °C for 3 h [165]. Subsequently, through the modification of SBA-15 and MCM-41 with H_2SO_4 , SBA-15- SO_3H and MCM-41- SO_3H were synthesized by Lai et al. [166] and Bai et al. [167]. By experimentation, they were determined to be more active than SBA-15 and MCM-41 in the hydrolysis of cellulose, leading to 52.0% glucose yield at 150 °C for 3 h and 47.2% TRS yield at 230 °C for 15 min in aqueous solution, respectively. More recently, Feng et al. reported a water-tolerant silica-supported perfluorobutylsulfonamide ($PSFSI-MSMA_{15}/SiO_2$) in 2014, which could also be used as a solid acid catalyst for the hydrolysis of cellulose in aqueous solution [168]. After 2 h, the yield of TRS with 67.0% was observed at a moderate reaction temperature of 120 °C.

3.6. Supported metals

The supported metal catalysts are known for their excellent hydrogenation activities and are widely employed in the transformation of biomass [169–171]. In recent years, considerable attention has been devoted to the conversion of cellulose into sugar alcohols over supported metals in the presence of acids, and in these processes, cellulose is firstly hydrolyzed into glucose by acids and the formed glucose is subsequently hydrogenated into sugar alcohols by supported metals [172–175]. However, as to the former step, the hydrolysis of cellulose into glucose is rarely catalyzed by supported metals. Gratifyingly, a breakthrough was achieved in 2010 by Kobayashi et al. and in his research, the mesoporous carbon-supported ruthenium (Ru/CMK-3) was found to be effective for the hydrolysis of cellulose into glucose without the aid of acids [176]. In order to explore the role of the support and metal, CMK-3 and various metal content of Ru/CMK-3 were studied at 230 °C for 15 min. When CMK-3 was used as a catalyst, the yields of glucose and oligosaccharides were 20.5% and 22.1%, suggesting that CMK-3 itself could catalyze the hydrolysis of cellulose in aqueous solution. In the presence of Ru on CMK-3, glucose yield increased from 27.6% to 34.2% when the content of Ru increased from 2.0% to 10.0%, whereas the yield of oligosaccharides decreased from 14.8% to 5.1%. Accordingly, the yield of TRS (glucose plus oligosaccharides) was kept at about 40.0%, which was independent



Scheme 9. Formation pathway of the active species $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ on CMK-3 [177].

of the content of Ru. As can be seen from these results, although CMK-3 and Ru are active for the hydrolysis of cellulose, the main role of CMK-3 is to transform cellulose into oligosaccharides and the main role of Ru is to convert oligosaccharides into glucose (Scheme 8). Therefore, the synergistic effect of CMK-3 and Ru as an acid catalyst should be responsible for the hydrolysis of cellulose into glucose. In the next year, by the analysis of XRD, small angle X-ray scattering (SAXS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and H_2 -temperature-programmed reduction (TPR), the active species of Ru was identified to $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$ that was formed by the reduction and passivation of RuCl_3 on CMK-3 (Scheme 9), which could give a Brønsted acid by the heterolysis of water molecule on Ru or give a Lewis acid by the dissociation of water molecule on Ru [177]. Moreover, it is important to point out that this novel method in the absence of acids provide a meritorious reference in the development of new supported metal catalysts for the hydrolysis of cellulose.

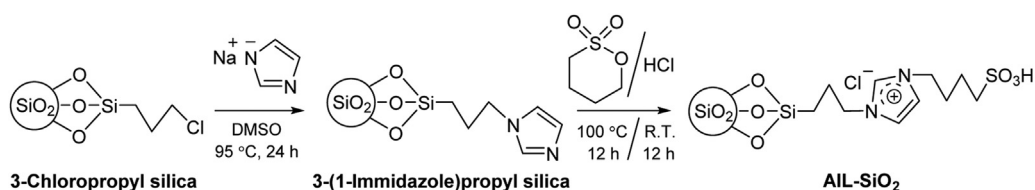
3.7. Immobilized acidic ionic liquids

To date, acidic ionic liquids such as 1-(1-propylsulfonic)-3-methylimidazolium chloride ($[\text{PSO}_3\text{HMIM}]\text{Cl}$) [178], 1-(1-butylsulfonic)-3-methylimidazolium chloride ($[\text{BSO}_3\text{HMIM}]\text{Cl}$) [179], 1-butyl-3-methylimidazolium hydrogen sulfate ($[\text{BMIM}]\text{HSO}_4$) [180] and triethyl-(3-sulfoethyl)-ammonium hydrogen sulfate ($[\text{TESPA}]\text{HSO}_4$) [181] have been successfully applied as catalysts for the hydrolysis of cellulose in the presence of $[\text{BMIM}]\text{Cl}$, resulting in excellent yields of TRS with 92.0–99.0% at a low reaction temperature of 70–100 °C for a short reaction time of 30–80 min. However, high cost, high viscosity and troublesome separation of these catalysts still hamper their practical applications. Consequently, the development of immobilized acidic ionic liquid catalysts is an urgent necessary for the economical and simple hydrolysis of cellulose. In 2014, Wiredu and Amarasekara synthesized a silica-immobilized imidazolium-type acidic ionic liquid (AIL- SiO_2) (Scheme 10), leading to 48.1% TRS yield in aqueous solution at 190 °C for 3 h, which was shown to be a better catalytic activity than *n*-propylsulfonic acid silica ($\text{PrSO}_3\text{H}-\text{SiO}_2$) and sulfonic acid silica ($\text{SO}_3\text{H}-\text{SiO}_2$) with 19.9% and 13.2% TRS yields under the same reaction conditions, respectively [182]. In the same year, a biochar sulfonic acid-immobilized chlorozincate ionic liquid ($\text{BC}-\text{SO}_3\text{H}-\text{IL}-\text{Zn}$) was prepared by Zhang et al. via a multistep process involving the synthesis of biochar sulfonic acid ($\text{BC}-\text{SO}_3\text{H}$) and 1-trimethoxysilylpropyl-

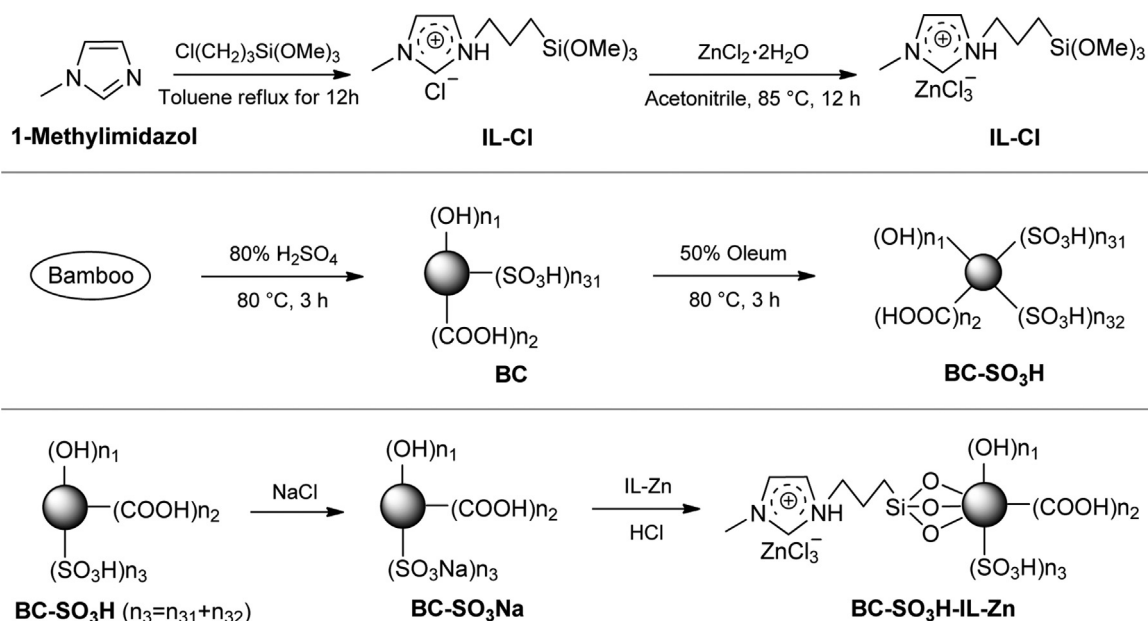
3-methylimidazolium zinc chloride ($\text{IL}-\text{Zn}$) and the grafting of $\text{IL}-\text{Zn}$ on $\text{BC}-\text{SO}_3\text{H}$ (Scheme 11) [183]. When $\text{BC}-\text{SO}_3\text{H}-\text{IL}-\text{Zn}$ was employed for the hydrolysis of cellulose in aqueous solution, 58.7% yield of TRS was obtained at 90 °C for 2 h. In comparison with $-\text{OH}$ groups of $\text{BC}-\text{SO}_3\text{H}$, the introduction of $\text{IL}-\text{Zn}$ groups that are the cellulose-binding sites could strengthen the affinity to cellulose and improve the acidity of $-\text{SO}_3\text{H}$ groups that are the cellulose-hydrolyzing sites. Hence, a good catalytic activity of $\text{BC}-\text{SO}_3\text{H}-\text{IL}-\text{Zn}$ for the hydrolysis of cellulose should be attributed to the synergistic effect between $\text{IL}-\text{Zn}$ groups and $-\text{SO}_3\text{H}$ groups.

3.8. Carbonaceous acids

Carbonaceous acids, as a novel type of solid acid catalysts, were firstly reported by Hara et al. in 2004 [184] and then used by Toda et al. in 2005 for the production of biodiesel [185]. Following their work, a great many of carbonaceous solid acid catalysts, which are generally prepared by the incomplete carbonization of natural organic matters and the subsequent sulfonation of the resulting amorphous carbons in the presence of concentrated sulfuric acid, fuming sulphuric acid or chlorosulfonic acid [186–195], have been designed for the hydrolysis of cellulose. For example, in 2008 and 2014, Onda et al. [140] and Zhao et al. [49] prepared an active carbon- ($\text{AC}-\text{SO}_3\text{H}$) and a graphene oxide-based ($\text{GO}-\text{ene}$) solid acid catalysts, resulting in 40.5% and 49.9% glucose yields in aqueous solution at 150 °C for 24 h, respectively. In 2012 and 2013, glucose- ($\text{GC}-\text{SO}_3\text{H}$) and sucrose-derived ($\text{SC}-\text{SO}_3\text{H}$) solid acid catalysts were also synthesized by Guo et al. [196] and Liu et al. [197], and when they were applied in the presence of $[\text{BMIM}]\text{Cl}$, the yields of TRS with 72.7% and 71.0% were obtained at 110 °C and 120 °C for 4 h, respectively. In contrast to the above-mentioned conventional solid acid catalysts such as Amberlyst-15, Sulf-Si/Zr/O, SBA-15- SO_3H and AIL- SiO_2 , carbonaceous solid acid catalysts possess carboxylic ($-\text{COOH}$) groups and phenolic $-\text{OH}$ groups as well as $-\text{SO}_3\text{H}$ groups, they are proved to have a strong ability to adsorb cellulose through the formation of hydrogen bonds with $-\text{OH}$ groups of cellulose [196–202]. That is, in the process of the hydrolysis of cellulose, once cellulose is adsorbed by $-\text{COOH}$ groups and phenolic $-\text{OH}$ groups and it will be readily hydrolyzed by $-\text{SO}_3\text{H}$ groups (Scheme 12). As a consequence, the synergic effect of $-\text{COOH}$ groups, phenolic $-\text{OH}$ groups and $-\text{SO}_3\text{H}$ groups should be the reason for the excellent catalytic activities of carbonaceous solid acid catalysts, which is also consistent with the lower activation energy. Moreover, because $-\text{Cl}$ groups also have a strong ability to adsorb cellulose via the similar manner to $-\text{COOH}$ groups and phenolic $-\text{OH}$ groups, hence, a new kind of carbonaceous solid acid catalysts such as sucralose-derived solid acid catalyst ($\text{SUCRA}-\text{SO}_3\text{H}$) [203], polyvinyl chloride-mixed starch-derived solid acid catalyst ($\text{PVC}-\text{SC}-\text{SO}_3\text{H}$) [204] and hydrochloric acid-pretreated cellulose-derived solid acid catalyst ($\text{HA}-\text{CC}-\text{SO}_3\text{H}$) [51] containing $-\text{Cl}$ groups and $-\text{SO}_3\text{H}$ groups were successfully prepared and used for the hydrolysis of cellulose in 2014, good results with 55.0% glucose yield, 94.2% TRS yield and 95.8% glucose selectivity were achieved in aqueous solution at 120 °C for 24 h, 120 °C for 6 h and 155 °C for 4 h, respectively.

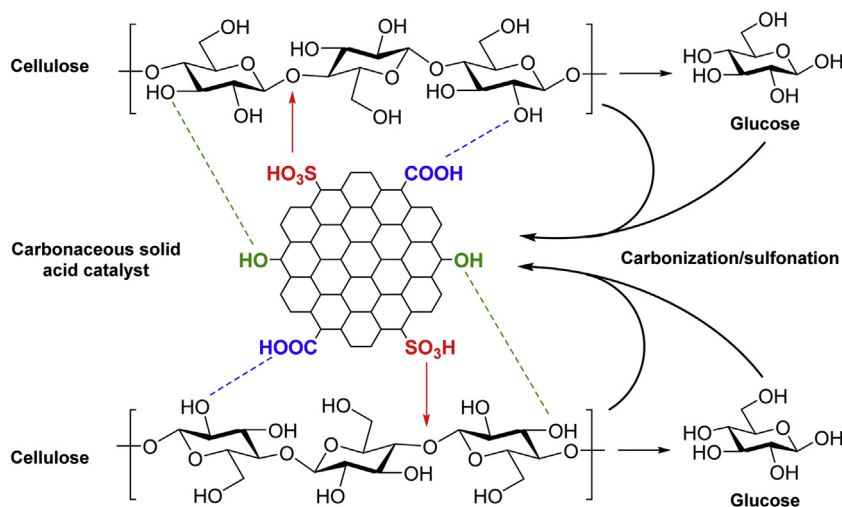


Scheme 10. Synthesis of $\text{AIL}-\text{SiO}_2$ [182].

Scheme 11. Synthesis of BC-SO₃H-IL-Zn [183].

Furthermore, it should be pointed out that much effort has been expended in the search for the neoteric carbonaceous solid acid catalysts, however, the effects of preparation conditions on these carbonaceous solid acid catalysts have rarely been investigated. Recently, Pang et al. found that the sulfonation temperature has a great impact on acid density and specific surface area of AC-SO₃H [17]. To be specific, the higher the sulfonation temperature, the higher the total acid density, when the sulfonation temperature increased from 150 °C to 300 °C, the total acid density accordingly increased from 0.8 mmol g⁻¹ to 2.19 mmol g⁻¹. In addition, with the increase of the sulfonation temperature in the range 150–250 °C, –SO₃H groups density and specific surface area increased from 0.19 mmol g⁻¹ to 0.24 mmol g⁻¹ and from 709 m² g⁻¹ to 945 m² g⁻¹, respectively, however, the corresponding values sharply decreased when the sulfonation temperature further increased to 300 °C. Moreover, the pretreatment of AC with HNO₃ prior to the sulfonation process led to an additional increase in the total acid density because treating the AC with HNO₃ also introduced some acidic functional groups such as –OH groups and/or –COOH groups, which could improve the catalytic activ-

ity of AC-SO₃H for the hydrolysis of cellulose. Thus, among a series of AC-SO₃H, AC-N-SO₃H-250 pretreated with HNO₃ and sulfonated at 250 °C gave the best results, a high yield of glucose with 62.6% was observed in aqueous solution at 150 °C for 24 h. Apart from the sulfonation temperature, Pang et al. also found that the types of carbon sources also have a large effect on the catalytic activities of carbonaceous solid acid catalysts [17]. In order to illustrate this issue, six carbon sources including acetylene carbon black (ACB), multiwall carbon nanotube (MWCNT), cellulose carbon (CC), resin carbon (RC), coconut shell active carbon (CSAC) and ordered mesoporous carbon (CMK-3) were tested, and the results indicated that the sulfonated CMK-3 exhibited the highest catalytic activity for the hydrolysis of cellulose, resulting in 74.5% glucose yield in aqueous solution at 150 °C for 24 h. In addition to a high acid density and a reasonable specific surface area, the sulfonated CMK-3 possessed a mesoporous carbon structure, facilitating the transportation of large molecules such as glucose, cellobiose and cellotriose in comparison with microporous carbons, which should be another reason for its remarkable catalytic activity. More convincingly, the advantages of mesoporous carbons as the catalyst supports have also



Scheme 12. Hydrolysis of cellulose into glucose over carbonaceous solid acid catalysts.

been demonstrated in hydrogenolysis of cellulose as well as the hydrolysis of cellulose [205].

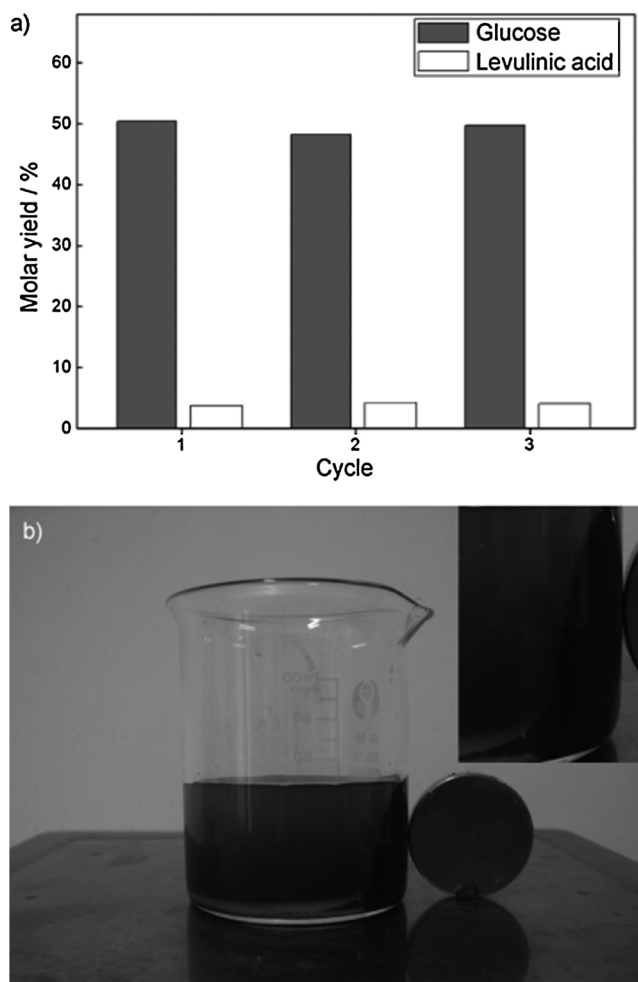
3.9. Magnetic acids

In the practical process for the hydrolysis of cellulose, the efficient separation of catalysts is very important to reduce the production costs and analyze the recyclabilities of catalysts. Although the above-mentioned solid acid catalysts are separable in theory, they are not easy to separate with the hydrolysis residues of cellulose. To address this problem, magnetic solid acid catalysts are preferable and desirable. In 2011, Lai et al. developed a sulfonated mesoporous silica-magnetite nanoparticle (Fe_3O_4 -SBA- SO_3H) by using a surfactant-templated sol-gel method, and when it was employed for the hydrolysis of cellulose in aqueous solution, the yield of glucose with 50.0% was obtained at 150 °C for 3 h [36]. Moreover, when cellobiose was used as a substrate, it also gave an excellent glucose yield up to 96.0% at 120 °C for 1 h, which was much higher than that over H_2SO_4 . A possible explanation is that the channels in Fe_3O_4 -SBA- SO_3H contained many acid sites and the uniform structures allowed the reactants to easily enter and interact with these acid sites, facilitating the hydrolysis of β -1,4-glycosidic linkages. Excitingly, after the first reaction run, Fe_3O_4 -SBA- SO_3H could be easily separated from the reaction mixtures by an external permanent magnet and reused for the next reaction run without an obvious loss of catalytic activity (Scheme 13). Following this work, a core-shell structure catalyst of

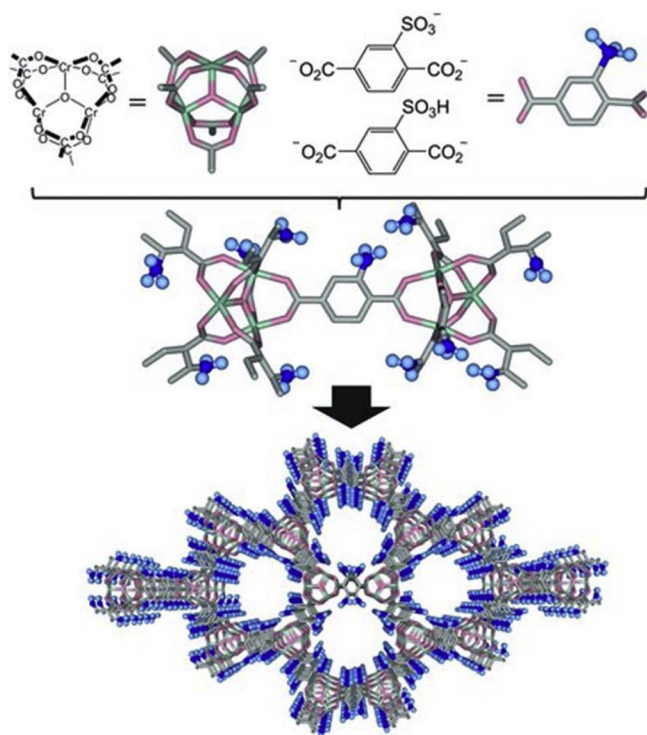
$\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-SO}_3\text{H}$ was prepared by the immobilization of $-\text{SO}_3\text{H}$ groups on the surface of SiO_2 -encapsulated Fe_3O_4 nanoparticle, and it showed a high catalytic activity for the hydrolysis of cellulose with 73.2% yield of TRS in the presence of [BMIM]Cl at 130 °C for 8 h [206]. Using an analogous method, Zhang et al. and Guo et al. synthesized a magnetic glucose-based carbonaceous solid acid catalyst ($\text{Fe}_3\text{O}_4@ \text{C-SO}_3\text{H}$) and a superparamagnetic cellulose-derived carbonaceous solid acid catalyst (PCM- SO_3H) with a core-shell structure, leading to 52.1% glucose selectivity with 48.6% cellulose conversion in aqueous solution at 140 °C for 12 h [207] and 68.9% yield of TRS in [BMIM]Cl at 130 °C for 3 h [37], respectively. More recently, a functionalized graphene oxide in combination with iron nanoparticle (Fe-GO- SO_3H) was reported by Verma et al. in 2013, and when it was applied for the hydrolysis of cellulose in aqueous solution, 50.0% glucose yield with 94.3% TRS yield was achieved at a low reaction temperature of 75 °C for 44 h [208]. The excellent catalytic activity of Fe-GO- SO_3H should be due to the water-soluble nanostructure of graphene oxide with a large concentration of $-\text{COOH}$ groups, phenolic $-\text{OH}$ groups and $-\text{SO}_3\text{H}$ groups.

3.10. Others

In addition to the above-mentioned solid acid catalysts, many other kinds of solid acid catalysts have also been developed for the hydrolysis of cellulose. For instance, Fang et al. and Zhang et al. prepared a hydrotalcite nanoparticle ($\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3$) in 2011 [209] and a calcium ferrite (CaFe_2O_4) in 2012 [210] via the co-precipitation method, and when they were used as solid acid catalysts for the hydrolysis of cellulose, 47.4% and 49.8% yields of TRS with 85.8% and 74.1% glucose selectivities were observed in aqueous solution at 150 °C for 24 h, respectively. More importantly, the two catalysts could be reused four times without much drop in the catalytic activities. Subsequently, a variety of acid-activated montmorillonite catalysts were reported by Tong et al. in 2013, and the results indicated that the montmorillonite treated by H_2SO_4 (SA-MMT) exhibited a higher conversion of cellulose up to 91.2% in aqueous solution at 200 °C for 4 h, while the montmorillonite treated by H_3PO_4 (PA-MMT) showed a higher yield of TRS with 16.9% under the same reaction conditions [211]. Recently, a new MIL-101-based porous coordination polymer (PCP) that is composed of a chromium oxide cluster and terephthalate ligands containing $-\text{SO}_3\text{H}$ groups (MIL-101-PCP- SO_3H) was synthesized by Akiyama et al. through a solvothermal reaction (Scheme 14), resulting in 1.4% and 1.2% yields of glucose and cellobiose in aqueous solution at 120 °C for 3 h, respectively [212]. As confirmed by ^1H NMR spectroscopy, 5-hydroxymethylfurfural (HMF), levulinic acid (LA) and FA, which are generally produced as the undesired side products after the hydrolysis of cellulose under the strongly acidic conditions, were not detected in this study. It is assumed that only one end of cellulose chain could enter into the pores of MIL-101-PCP- SO_3H and contact with acidic sites, leading to a clean and selective cut of the cellulose chain [212]. Furthermore, it should be pointed out that the hydrolysis efficiency depended on the contact time and frequency between cellulose and acidic sites, which was enhanced by micropores that could trap cellulose. However, further investigations are necessary to explore the mechanism of this process. More recently, Qian et al. designed a novel ceramic membrane-based solid acid catalyst (PIL-CM-PSSA) (Scheme 15), and it consisted of a poly(vinyl imidazolium chloride) ionic liquid (PIL) polymer chain that was synthesized by the UV-initiated free radical polymerization (UFRP) and a poly(styrene sulfonic acid) (PSSA) polymer chain that was synthesized by the surface initiated atom-transfer radical polymerization (ARTP), which were used for the dissolution of cellulose and the hydrolysis of cellulose, respectively [63]. When the reaction was conducted in the presence of [EMIM]Cl and aqueous solution, the yields of TRS with 97.4% and



Scheme 13. Reuse (a) and separation (b) of Fe_3O_4 -SBA- SO_3H [36].



Scheme 14. Schematic representation of the structure of MIL-101-PCP-SO₃H [212].

32.7% were reached at 130 °C for 6 h and 140 °C for 48 h, respectively. More interestingly, the catalytic activity of PIL-CM-PSSA can be tuned by varying chain length and chain density of polymer branches grafted on CM, which is a big advance in the development of solid acid catalysts.

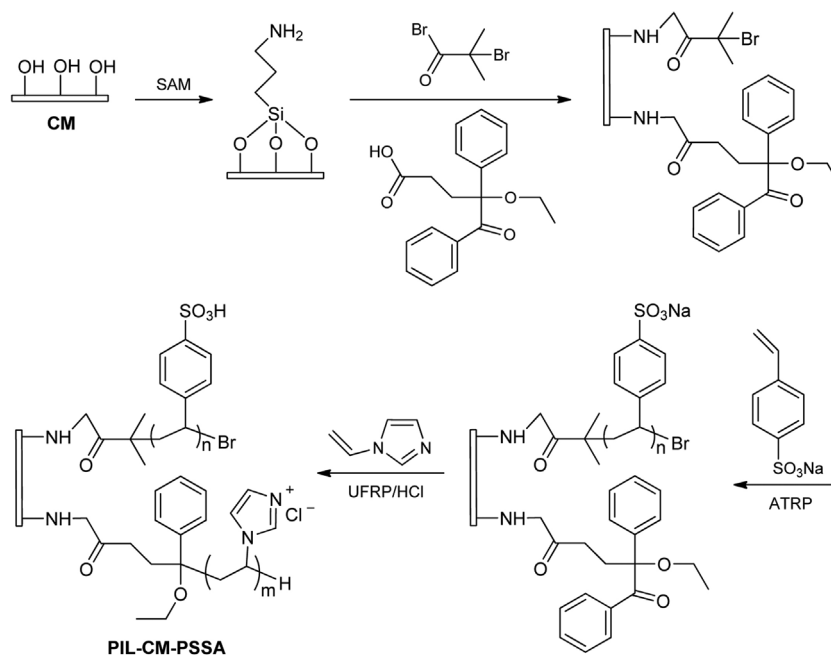
4. Auxiliary methods for the hydrolysis of cellulose

In order to destroy the crystalline structure of cellulose, increase the contact area of cellulose with catalysts and improve the hydroly-

sis efficiency of cellulose, some effective auxiliary methods have been proposed in recent years. In the following part, the common pretreatment techniques such as dissolution/regeneration, ball-milling, ultrasound and non-thermal atmospheric plasma (NTAP) and advanced heating methods such as microwave irradiation are discussed in detail (Table 2).

4.1. Pretreatment techniques

As stated in the second part, cellulose is soluble in ionic liquids and insoluble in water and most organic liquids. Therefore, in the pretreatment process of dissolution/regeneration, ionic liquids are generally used as the solvents for the dissolution of cellulose and water or organic liquids are universally used as the antisolvents for the regeneration of cellulose [87]. According to the experiment results, molecular dynamics simulations and ab-initio calculations in the previous literatures, when cellulose is dissolved in ionic liquids such as [EMIM]Cl, [EMIM]OAc, [BMIM]Cl and [BMIM]OAc, the addition of antisolvents such as water, ethanol and acetone leads to the destruction of hydrogen bonds between cellulose and ionic liquids and the subsequent formation of hydrogen bonds between antisolvents and ionic liquids and between cellulose and cellulose, resulting in the regeneration of cellulose from ionic liquids [213–218]. Moreover, the stronger the interactions between antisolvents and ionic liquids, the easier the regeneration of cellulose from ionic liquids [80]. Due to the strongest binding energies between water and ionic liquids, hence, water is regarded as the most effective antisolvents [215]. More excitingly, after the pretreatment of dissolution/regeneration, several dramatic changes in the structure, morphology and size of cellulose can be observed from crystalline state, smooth appearance and long chain to amorphous state, porous appearance and short chain (as confirmed by XRD and scanning electron microscope (SEM)), respectively, showing a much more accessible surface that can enhance the catalytic activities of catalysts [36,88,121,166,203,210]. For example, in 2014, Morales-de-laRosa et al. found that when the original cellulose was used as a substrate in aqueous solution, only 20.0% glucose yield with 24.0% cellulose conversion was obtained in the presence of H₃PW₁₂O₄₀ at 140 °C for 5 h, however, when the regenerated



Scheme 15. Synthesis of PIL-CM-PSSA [63].

Table 2
Hydrolysis of cellulose through various auxiliary methods^a.

Catalyst	Pretreatment method	Solvent	Catalyst loading (%)	Cellulose concentration (%)	Temperature (°C)	Time (h)	TRS yield (%)	Glucose yield (%)	References
H ₃ PW ₁₂ O ₄₀	–	H ₂ O	108.4 ^b	1.0	140	5	–	20.0	[106]
H ₃ PW ₁₂ O ₄₀	DR	H ₂ O	108.4 ^b	1.0	140	5	–	89.0	[106]
K26	SM	HCl solution	15.4	0.8	180	1/3	–	30.0	[219]
K26	MM	HCl solution	15.4	0.8	180	1/3	–	88.0	[219]
K26	SM	H ₂ O	15.4	0.8	180	1/3	12.9	–	[220]
K26	MM	H ₂ O	15.4	0.8	180	1/3	90.0	–	[220]
AC-SO ₃ H	US	H ₂ O	100.0	10.0	150	1	–	15.1	[234]
Amberlyst-35	NTAP	H ₂ O	40.0	10.0	150	1	–	22.0	[235]
HY	–	[BMIM]Cl	10.0	5.0	100	10	–	2.1	[241]
HY	MW	[BMIM]Cl	10.0	5.0	100	2/15	–	36.9	[241]
H ₃ PW ₁₂ O ₄₀	MW	H ₂ O	2132.4 ^b	2.0	90	3	–	75.6	[38]
NO catalyst	MW	H ₂ O	–	10.0	220	1/60	–	11.0	[242]

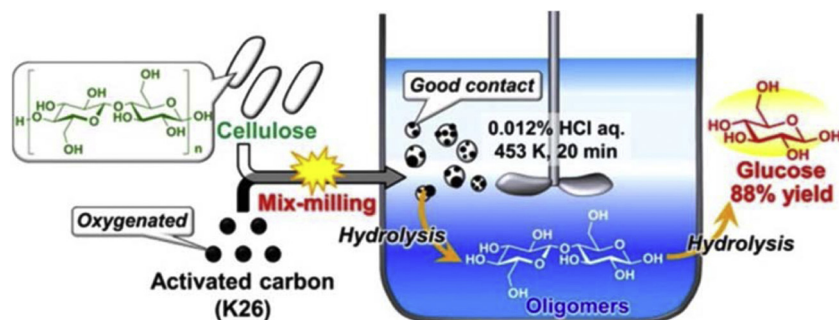
^a DR, SM, MM, US and MW are representative of dissolution/regeneration, single-milling, mix-milling, ultrasound and microwave irradiation, catalyst loading and cellulose concentration are relative to the mass of cellulose and the mass of solvent, respectively.

^b Catalyst loading is relative to the mole of glucose units in cellulose.

cellulose pretreated with [EMIM]Cl and water was used as a substrate, up to 89.0% glucose yield with 98.0% cellulose conversion was achieved under the same reaction conditions [106]. In addition, it is noteworthy that this pretreatment technique allows the recovery of the applied ionic liquids, which is a critical to reduce the production costs.

Similarly, ball-milling is also a frequently-used technique for the pretreatment of cellulose, which can decrease the crystallinity of cellulose and then increase the yield of glucose [17,124,131,140,164,176,207,212]. More interestingly, the patterns of ball-milling have a great impact on the hydrolysis of cellulose. In 2013, Kobayashi et al. reported that the mix-milling of cellulose and catalyst (K26) with alumina balls (Scheme 16) was more active than the single-milling of cellulose with alumina balls, and when the two pretreated cellulose were hydrolyzed in dilute hydrochloric acid solution, 98.0% cellulose conversion with 88.0% glucose yield and 40.0% cellulose conversion with 30.0% glucose yield were obtained at 180 °C for 20 min, respectively [219]. For a better understanding of the role of mix-milling, three types of combinations including (1) cellulose and K26, (2) cellobiose and K26, and (3) cellulose and benzoic acid were investigated by Yabushita et al. in 2014, the results demonstrated that only the combination of cellulose and K26 drastically enhanced the hydrolysis efficiency, the yield of TRS increased seven times from 12.9% to 90.0% at 180 °C for 20 min, indicating that the predominant role of mix-milling was the improvement of solid–solid contact area between cellulose and catalyst not the mechanocatalytic hydrolysis [220]. Furthermore, it should be pointed out that although ball-milling including single-milling and mix-milling is a promising pretreatment technique for promoting the hydrolysis of cellulose, it needs to spend a long pretreatment time (24–96 h) to achieve the desired results, which is energy-intensive in contrast to the technique of dissolution/regeneration.

Compared to the above-mentioned dissolution/regeneration and ball-milling, ultrasound is a novel pretreatment technique of cellulose. The effects of ultrasound are the consequence of the cavitation phenomenon involving the formation, growth and collapse of microbubbles in the liquid phase [221]. By imploding, these microbubbles can create the locally high pressure (up to 1000 bar) and temperature (up to 5000 °C), leading to high-energy radical mechanisms and interesting physicochemical functions [222], hence, ultrasound-assisted pretreatment of cellulose has attracted much attention in recent years [223–230]. In 2007 and 2009, Mikkola et al. [231] and Sun et al. [232] reported that an ultrasonic pretreatment could improve the solubility of cellulose in [AMIM]Cl and [EMIM]OAc, respectively, which was ascribed to that ultrasonic pretreatment could destroy the hydrogen bonds of cellulose and then facilitate the penetration and diffusion of ionic liquids into the structure of cellulose [233]. Subsequently, Lan et al. found that with the increase of ultrasonic power from 20 W to 50 W and irradiation time from 0 to 20 min, the dissolution time of cellulose in [BMIM]Cl decreased from 147 min to 100 min and from 190 min to 60 min, respectively. More recently, the effects of ultrasonic pretreatment on the structure of cellulose were studied by Zhang et al. in 2013 via the use of various characterization methods, the results suggested that although the crystallinity of cellulose was not significantly affected by ultrasound, the size of cellulose drastically decreased from 38 μm to less than 0.4 μm, resulting in a better interaction with catalyst [234]. Satisfactorily, using such a pretreatment, the hydrolysis of cellulose in aqueous solution over AC-SO₃H produced 15.1% glucose yield at 150 °C for 1 h, which was similar to those obtained by the pretreatment techniques of dissolution/regeneration and ball-milling. From the viewpoint of green and sustainable chemistry, the ultrasound-assisted pretreatment of cellulose has several noticeable advantages such as the use of water as a sole solvent, a short pretreatment time (<3 h), no exter-



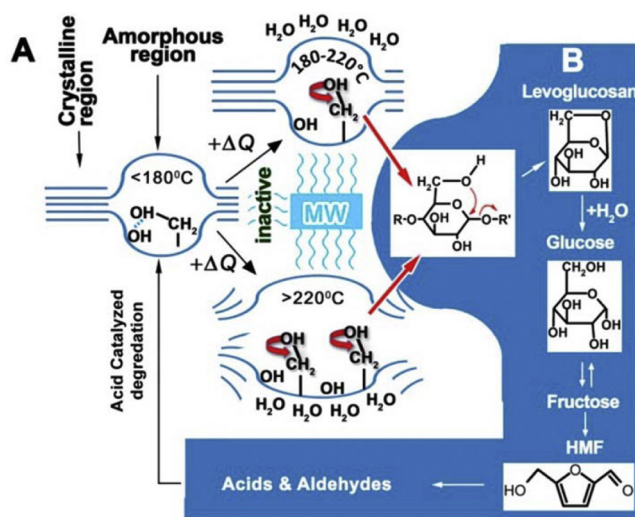
Scheme 16. Hydrolysis of cellulose via a mix-milling pretreatment [219].

nal source of heating is needed and no contamination is introduced or produced.

In addition to ultrasound, NTAP is another novel technique for the pretreatment of cellulose, which was developed by Benoit et al. in 2011 [235]. In their experiments, cellulose with a DP of 200 was placed in two parallel square copper electrodes and the copper electrodes were spaced by 2 mm to assure an optimal plasma discharge, in which NTAP was formed by using a pulsed voltage waveform at a maximum voltage of 11.2 kV at the frequency of 2 kHz and the power was continuously maintained at 26 W. Remarkably, under the dielectric material of air, the DP of cellulose was dramatically decreased to 120 after 3 h, which was conducive for a better dispersion of cellulose in aqueous solution, thereby increasing its interaction with a solid acid catalyst. When the pretreated cellulose was hydrolyzed by the catalyst of Amberlyst-35, the yield of glucose with 22.0% was obtained at 150 °C for 1 h, which was much higher than that obtained by the pretreatment techniques of dissolution/regeneration and ball-milling, meaning that NTAP was more efficient than dissolution/regeneration and ball-milling for the pretreatment of cellulose [235]. Moreover, in order to get more insight on the functional mechanism of NTAP, the influence of water and composition of air on the efficiency of NTAP was further studied by Benoit et al. in 2012 [236]. The results indicated that whether air was wet or dry, no impact on the efficiency of NTAP was observed, suggesting that the moisture of air did not play a crucial role in the pretreatment of cellulose. When oxygen content in the presence of nitrogen was increased from 20 wt% to 70 wt%, the hydrolysis of cellulose was inhibited, showing that a ratio of oxygen and nitrogen with 20 wt% close to that of air was optimal for the pretreatment of cellulose with NTAP, which clearly demonstrated that oxynitrides (NO_x) produced in NTAP should be the active species in the pretreatment of cellulose and it might participate in the activation of water contained in cellulose [236]. However, how oxynitrides activate water is worth investigating in the future. More importantly, Benoit et al. also found that when NTAP was used together with ball-milling, the DP of cellulose was further decreased to 36. As expected, the pretreated cellulose with a lower DP was more prone to be hydrolyzed into glucose with an unprecedented yield of 58.0% over a solid acid catalyst of Amberlyst-35 at 150 °C for 1 h, which was one of the highest yields of glucose ever obtained in aqueous solution [236]. Hence, it is convinced that the combination of various pretreatment techniques will undoubtedly contribute to provide a promising technique for the pretreatment of cellulose in a rational way.

4.2. Advanced heating methods

Previously, the hydrolysis of cellulose was mainly carried out with conventional heating methods such as oil-bath and sand-bath. However, these methods, which are based on the convective–conductive heating from the surface into the interior of the reaction systems, have several drawbacks such as slow heating rate, high energy-consumption and non-uniform heating [237]. In contrast, microwave irradiation produces the internal heating of the reaction systems by the direct coupling of microwave energy with solvents, substrates and catalysts, which can overcome the drawbacks of conventional heating methods [238–240]. Thus, in recent years, microwave irradiation has been gradually applied for the hydrolysis of cellulose. In 2009, Zhang and Zhao found that when the hydrolysis of cellulose was performed in an oil-bath, the yield of glucose was only 2.1% in the presence of [BMIM]Cl and HY at 100 °C for 10 h, while the corresponding value markedly increased to 36.9% in the ultrashort reaction time of 8 min when microwave irradiation was used as a heating method [241]. More convincingly, the same trend was reported in 2012 by Li et al., when $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was employed as a catalyst, an excellent glu-



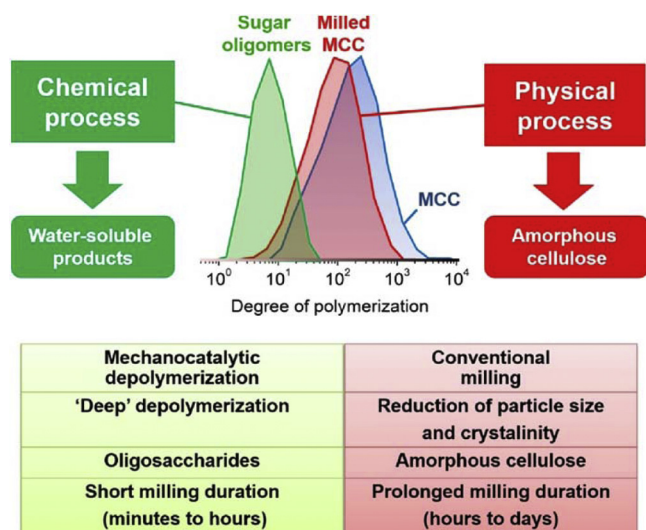
Scheme 17. Representation of the cellulose–microwave interaction as a function of temperature: (A) —OH group activation and (B) cellulose hydrolysis [242].

cose yield of 75.6% was achieved in aqueous solution at 90 °C for 3 h under the heating method of microwave irradiation [38], which was much higher than 50.5% by using the same catalyst in an oil-bath at 180 °C for 2 h [152]. As can be seen from these results, the usage of microwave irradiation is helpful to not only reduce the reaction time but also improve the yield of glucose compared to conventional heating methods. Furthermore, a systematic investigation of the interaction between microwave irradiation and cellulose has been carried out by Fan et al. in 2013 [242], the results indicated that —OH groups in cellulose were confirmed to be crucial for the hydrolysis of cellulose in the presence of microwave irradiation. Below the temperature of 180 °C, —OH groups were hindered from interacting with microwave irradiation, because they were strongly involved in the hydrogen bonds of cellulose within the amorphous and crystalline regions. However, above the temperature of 180 °C, —OH groups could be involved in the localized rotation that was caused by microwave irradiation. More importantly, the polar —OH groups would be similarly acted as the “molecular radiators”, initiating the selective cleavage of cellulose. In view of the limited presence of water in cellulose, it was likely to lead to the collisions between —OH groups and anomeric C1 of the same ring of glucose thus forming levoglucosan (Scheme 17), which could be easily hydrolyzed into glucose. Even without the addition of any catalyst, the yield of glucose could also be reached to 11.0% with a high selectivity of 75.0% at 220 °C for a very short time of 1 min [242]. On the basis of this work, it is concluded that cellulose can be hydrolyzed by only moderating the temperature under the heating method of microwave irradiation, making it more industrially favorable. With the development of science and technology, large microwave equipment may also be applied to the practical hydrolysis of cellulose, which will contribute to the large-scale production of chemicals and fuels.

5. Neoteric strategies for the hydrolysis of cellulose

5.1. Mechanocatalytic approach

In 2010, Hick et al. developed a new approach (mechanocatalysis) on the basis of mechanical processing for the hydrolysis of cellulose in the presence of solid acid catalysts and in the absence of solvents [243]. The results indicated that the natural layered structure of clays was ideally suited as a catalyst in such a mechanocatalysis process, mainly because the layers in clays



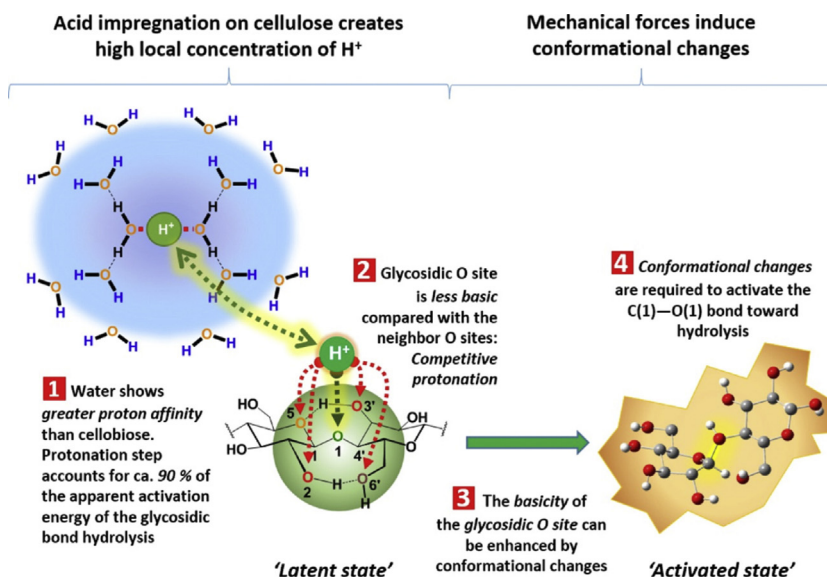
Scheme 18. Comparison of ball-milling and mechanocatalysis of cellulose [244].

are typically held by the weak forces such as hydrogen bonds and van der Waals forces, which can be easily broken by grinding and rubbing, leading to an increase in catalytic sites and a better contact with cellulose. Among a range of layered clays, kaolinite was the most active, after 3 h, up to 84.0% cellulose could be hydrolyzed in a single pass. Noteworthy, unlike conventional pretreatment technique of ball-milling, this strategy is a chemical process (Scheme 18), which can greatly reduce the energy input while concomitantly assuring the cleavage of β -1,4-glycosidic linkages [244–246]. In 2012, Meine et al. reported a significant improvement in mechanocatalytic strategy, in which the process began with the impregnation of cellulose with a strong acid such as H_2SO_4 or HCl followed by a solvent-free solid-state reaction, resulting in a complex mixture of oligosaccharides that are more reactive than cellulose [247]. Because mechanical processing did not destroy the acid catalyst, water-soluble oligosaccharides could be further hydrolyzed in aqueous solution, the yield of glucose with 91.0% was achieved at 130°C for 1 h. As a consequence, compared to the layered kaolinite, the acid-assisted mechanocatalytic hydrolysis of cellulose is more complete, faster and selective.

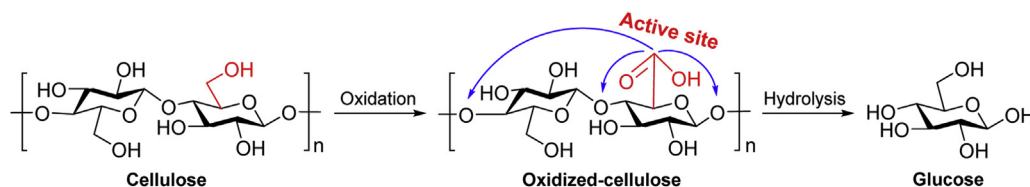
Subsequently, Schüth et al. proposed that the hydrolysis of acid-impregnated cellulose heavily depended on the conformational changes from latent state to activated state under the mechanical forces (Scheme 19), which is necessary for the cleavage of β -1,4-glycosidic linkages [244]. Conclusively, it should be pointed out that mechanocatalysis that is the combination of acid-catalysis with mechanical forces is a highly efficient approach to overcome the recalcitrance of cellulose, opening up a new horizon for the hydrolysis of cellulose.

5.2. Oxidation–hydrolysis approach

It is reported that $-\text{COOH}$ groups on cellulose possess the activation and inductive effects on the cleavage of β -1,4-glycosidic linkages in cellulose [248–251]. According to this phenomenon, an oxidation–hydrolysis strategy was developed by Zhou et al. in 2015 [252], in which partial hydroxymethyl ($-\text{CH}_2\text{OH}$) groups of glucose units of cellulose were firstly converted into $-\text{COOH}$ groups by a preoxidation step and then the generated $-\text{COOH}$ groups could be served as the active sites for the hydrolysis of cellulose (Scheme 20). Among various oxidants such as hydrogen peroxide (H_2O_2), potassium permanganate (KMnO_4), nitrogen dioxide (NO_2), oxygen (O_2), air, sodium nitrite–nitric acid ($\text{NaNO}_2\text{--HNO}_3$) and 2,2,6,6-tetramethylpiperidinoxy–sodium hypochlorite (TEMPO--NaClO), $\text{NaNO}_2\text{--HNO}_3$ that could in-situ generate NO_2 was found to be the most efficient, which was also reported by Zimmitsky et al. in 2004 [253] and Milichovsky et al. in 2007 [254]. Moreover, the preoxidation temperature displayed a significant effect on the amount of $-\text{COOH}$ groups. When the temperature was below 150°C , the preoxidation of cellulose did not occur, which would proceed to some extent at 180°C . However, when the temperature was elevated to 210°C , the amount of $-\text{COOH}$ groups were reached to a maximum. To further disclose the role of $-\text{COOH}$ groups in the cleavage of β -1,4-glycosidic linkages for the hydrolysis of cellulose, the theoretical calculations were carried out. The results suggested that the nearest β -1,4-glycosidic linkage was cleaved via a six-membered ring structure without the participation of water. However, due to the long distance between the other β -1,4-glycosidic linkage and $-\text{COOH}$ group, the cleavage of these linkages should involve water. Using such a strategy, 25.2% glucose yield with 65.5% glucose selectivity was obtained at 170°C for 8 h [252]. Furthermore, it is noteworthy that the oxidation–hydrolysis strategy is a self-



Scheme 19. Conformational changes of cellulose by mechanocatalysis [244].



Scheme 20. Hydrolysis of cellulose through an oxidation–hydrolysis strategy [252].

catalysis green process, in which an additional solid acid catalyst or homogeneous acid catalyst is not necessary and the problems relating to the utilization of catalysts can also be avoided.

6. Summary and outlook

So far in this review, we have summarized and discussed a sequence of reaction medias, auxiliary methods and mechanocatalytic approaches in addition to various types of solid acid catalysts for the hydrolysis of cellulose in recent years. Although many exciting results were achieved, it should be noted that the selective and massive hydrolysis of cellulose into glucose especially in aqueous solution is still enigmatic and atelic. In order to accelerate the industrialization process, some potential points should be addressed in the future studies: (1) The intensive investigation of the role of water. A very small amount of water can slow the hydrolysis of cellulose because water is a reactant, but too much water can also slow the hydrolysis of cellulose, supposedly because of the hydration of the acid sites on solid acid catalysts, which remains to be proved. (2) The innovative development of ionic liquids. Ionic liquids are not only the common reaction medias for the hydrolysis of cellulose but also the appropriate solvents for the pretreatment of cellulose. Theoretically, the types of ionic liquids are infinite, however, in the viewpoint of practical application, more cheaper, less corrosive, lower viscous and biodegradable ionic liquids are urgently needed. (3) The collaborative utilization of pretreatment techniques and microwave irradiation. The usage of pretreatment techniques can improve the hydrophilic accessibility of cellulose and different pretreatment techniques have different advantages. Moreover, the application of microwave irradiation can speed up the hydrolysis rate of cellulose to a large extent. Therefore, the combination of pretreatment techniques and microwave irradiation may be more active for the hydrolysis of cellulose. (4) The strategic preparation of multifunctional solid acid catalysts. Mass transfer limitation between cellulose and solid acid catalysts are the main bottleneck for the hydrolysis of cellulose. Conceptually, solid acid catalysts containing strong binding sites, strong acid sites, high specific surface areas and proper pore sizes are prone to display good catalytic activities. Thus, multifunctional solid acid catalysts with biomimetic selectivity and specific porosity as well as magnetic separability are necessary for the efficient hydrolysis of cellulose. (5) The comprehensive simulation of reaction mechanisms and hydrolysis processes. Considering the vast number of possible solid acid catalysts and reaction medias, the qualitative analysis of reaction mechanisms and quantitative description of hydrolysis processes are very time-consuming. To a certain extent, these challenges can be solved by the computational simulation, which will also supply a more accurate and reliable reference for the optimization of various reaction conditions. (6) The systematic design of consecutive reactor. Whichever hydrolysis approach is adopted, a consecutive reactor involving the pretreatment and hydrolysis of cellulose and the separation and recycle of catalyst should be designed in agreement with practical situation. All in all, the hydrolysis of cellulose, no matter which chemical or fuel is produced from glucose, should be moved in the direction of green, simple, efficient and inexpensive way, and the research on reaction

medias, catalyst types, auxiliary techniques, neoteric strategies and production equipments should also be further enhanced.

In our opinion, the present studies on the hydrolysis of cellulose have come to a critical period. From now on, we must redouble our efforts in expanding current technologies and learning from previous experiences and then apply them to the hydrolysis of cellulose to pave the way to a widespread implementation of biorefinery, where amazing happens!

Acknowledgements

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